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TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY

by

E. K. U. Gross and W. Kohn

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Department of Physics

University of California, Santa Barbara

Santa Barbara, CA 93106

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Time-dependent density functional theory as a complete formalism is of more recent origin. A detailed description of time-dependent density-functional formalism is presented with emphasis on evolving applications.

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TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY

E.K.U. Gross

W. Kohn

Department of Physics
University of California
Santa Barbara, CA 93106

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1. INTRODUCTION

Density functional theory for stationary states or ensembles is a formulation of many-body theory in terms of the particle density, $\rho(\mathbf{r})$. Based on the work of Hohenberg and Kohn¹ (HK) and Kohn and Sham² (KS), it is now a mature subject which has had many successful applications. In retrospect, the stationary Thomas-Fermi theory^{3,4} and the Hartree⁵ and Hartree-Fock-Slater⁶ equations can be viewed as approximations of density functional theory.

Time-dependent density functional theory as a complete formalism⁷ is of more recent origin, although a time-dependent version of Thomas-Fermi theory was proposed as early as 1933 by Bloch.⁸ The time-dependent Thomas-Fermi model provides good first estimates for a variety of physical processes such as atomic⁹⁻¹¹ and nuclear^{12,13} collisions, nuclear giant resonances,¹⁴⁻¹⁶ atomic photoabsorption,¹⁷⁻¹⁹ and plasmons in inhomogeneous media.²⁰⁻²⁵ The time-dependent Hartree and Hartree-Fock equations²⁶ have been used extensively for more quantitative studies of nuclear dynamics^{27,28} and atomic²⁹⁻³² as well as molecular³³ collision processes. However these methods neglect correlation effects. Inclusion of such effects would require the time-dependent analog of the stationary KS equations.

The first, and rather successful, steps towards a time-dependent KS theory were taken by Peuckert³⁴ and by Zangwill and Soven.³⁵ These authors treated the linear density response of rare-gas atoms to a time-dependent external potential as the response of non-interacting electrons to an effective time-dependent potential. In analogy to stationary KS theory, this effective potential was assumed to contain an exchange-correlation part, $v_{xc}(\mathbf{r}t)$, in addition to the time-dependent external and Hartree terms:

$$v_{eff}(\mathbf{r}t) = v(\mathbf{r}t) + \int \frac{\rho(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} d^3r' + v_{xc}(\mathbf{r}t).$$

Peuckert suggested an iterative scheme for the calculation of v_{xc} , while Zangwill and Soven adopted the functional form of the static exchange-correlation potential,

$$v_{xc}(\mathbf{r}t) = \frac{\delta E_{xc}[\rho(\mathbf{r}'t)]}{\delta \rho(\mathbf{r}t)},$$

where $E_{xc}[\rho]$ is the exchange-correlation energy functional of ordinary density functional theory. For this functional, Zangwill and Soven employed the local density approximation,

$$E_{xc}[\rho(\mathbf{r}'t)] = \int \epsilon_{xc}(\rho(\mathbf{r}'t)) \rho(\mathbf{r}'t) d^3 r',$$

where $\epsilon_{xc}(\rho)$ is the exchange-correlation energy per particle of a static uniform electron gas of density ρ . The static approximation is obviously valid only if the time-dependence of $\rho(\mathbf{r}t)$ is sufficiently slow. In practice, however, it gave quite good results even for the case of rather rapid time-dependence.

Significant steps towards a rigorous foundation of time-dependent density functional theory were taken by Deb and Ghosh³⁶⁻³⁹ and by Bartolotti⁴⁰⁻⁴³ who formulated and explored Hohenberg-Kohn and Kohn-Sham type theorems for the time-dependent density. Each of these derivations, however, was restricted to a rather narrow set of allowable time-dependent potentials (to potentials periodic in time in the theorems of Deb and Ghosh, and to adiabatic processes in the work of Bartolotti).

Finally, a general formulation covering essentially all time-dependent potentials of interest was given by Runge and Gross.⁷ A novel feature of this formalism, not present in ground-state density functional theory, is the dependence of the respective density functionals on the initial (many-particle) state $\Psi(t_0)$. A detailed description of the time-dependent density-functional formalism will be presented in section

2. The central result is a set of time-dependent KS equations which are structurally similar to the time-dependent Hartree equations but include (in principle exactly) all many-body correlations through a local time-dependent exchange correlation potential.

To date, most applications of the formalism fall in the regime of linear response. In section 3, we shall describe the linear-response limit of time-dependent density functional theory along with applications to the photo-response of atoms, molecules and metallic surfaces.

Beyond the regime of linear response, the description of atomic and nuclear collision processes appears to be a promising field of application where the time-dependent KS scheme could serve as an economical alternative to time-dependent configuration-interaction calculations.⁴⁴⁻⁴⁹ So far, only a simplified version of the time-dependent KS scheme has been implemented in this context.⁵⁰⁻⁵³

Another possible application beyond the regime of linear response is the calculation of atomic multiphoton ionization which, in the case of hydrogen, has recently been found^{54,55} to exhibit chaotic behaviour. A full-scale numerical solution of the time-dependent Schrödinger equation for a hydrogen atom placed in strong time-dependent electric fields has recently been reported.⁵⁶ A time-dependent Hartree-Fock calculation has been achieved for the multiphoton ionization of helium.⁵⁷ For heavier atoms an analogous solution of the time-dependent Kohn-Sham equations offers itself as a promising application of time-dependent density functional theory.

2. FORMAL FRAMEWORK

2.1. One-to-one mapping between time-dependent potentials and time-dependent densities

Density functional theory is based on the existence of an exact mapping between densities and external potentials. In the ground-

state formalism,¹ the existence proof relies on the Rayleigh-Ritz minimum principle for the energy. Straightforward extension to the time-dependent domain is not possible since a minimum principle is not available in this case. The proof given by Runge and Gross⁷ for time-dependent systems is based directly on the Schrödinger equation*

$$i \frac{\partial}{\partial t} \Psi(t) = \hat{H}(t) \Psi(t). \quad (1)$$

We shall investigate the densities $\rho(\mathbf{r}t)$ of electronic systems evolving from a fixed initial (many-particle) state

$$\Psi(t_0) = \Psi_0 \quad (2)$$

under the influence of different external potentials of the form

$$\hat{V}(t) = \sum_{\sigma=\uparrow\downarrow} \int d^3r \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) v(\mathbf{r}t) \hat{\psi}_{\sigma}(\mathbf{r}). \quad (3)$$

In the following discussion, the initial time t_0 is assumed to be finite and the potentials are required to be expandable in a Taylor series about t_0 :

$$v(\mathbf{r}t) = \sum_{j=0}^{\infty} \frac{1}{j!} v_j(\mathbf{r})(t - t_0)^j. \quad (4)$$

No further assumptions concerning the size of the radius of convergence are made. It is sufficient that the radius of convergence is greater than zero. The initial state Ψ_0 is not required to be the ground state or some other eigenstate of the initial potential $v(\mathbf{r}t_0) = v_0(\mathbf{r})$. This means that the case of sudden switching is included in the formalism. On the other hand, potentials that are switched-on adiabatically from $t_0 = -\infty$ are excluded by the condition (4).

* Atomic units are used throughout.

Besides an external potential of the form (3), the Hamiltonian in Eq. (1) contains the kinetic energy of the electrons and their mutual Coulomb repulsion:

$$\hat{H}(t) = \hat{T} + \hat{U} + \hat{V}(t) \quad (5)$$

with

$$\hat{T} = \sum_{\sigma=\uparrow\downarrow} \int d^3r \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \hat{\psi}_{\sigma}(\mathbf{r}) \quad (6)$$

and

$$\hat{U} = \frac{1}{2} \sum_{\sigma, \tau} \int d^3r \int d^3r' \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\tau}^{\dagger}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \hat{\psi}_{\tau}(\mathbf{r}') \hat{\psi}_{\sigma}(\mathbf{r}). \quad (7)$$

The number of electrons, N , is fixed.

We shall demonstrate in the following that the densities $\rho(\mathbf{r}t)$ and $\rho'(\mathbf{r}t)$ evolving from a common initial state Ψ_0 under the influence of two potentials $v(\mathbf{r}t)$ and $v'(\mathbf{r}t)$ are always different provided that the potentials differ by more than a purely time-dependent (\mathbf{r} -independent) function:[†]

$$v(\mathbf{r}t) \neq v'(\mathbf{r}t) + c(t). \quad (8)$$

Since both potentials can be expanded in a Taylor series and since they differ by more than a time-dependent function, some of the expansion coefficients $v_j(\mathbf{r})$ and $v'_j(\mathbf{r})$ (cf. Eq. (4)) must differ by more than

[†] If v and v' differ by a purely time-dependent function, the resulting wave functions $\Psi(t)$ and $\Psi'(t)$ differ by a purely time-dependent phase factor and, consequently, the resulting densities ρ and ρ' are identical. This trivial case is excluded by the condition (8), in analogy to the ground-state formalism where the potentials are required to differ by more than a constant.

a constant. Hence there exists some smallest integer $k \geq 0$ such that

$$v_k(\mathbf{r}) - v'_k(\mathbf{r}) = \frac{\partial^k}{\partial t^k} [v(\mathbf{r}t) - v'(\mathbf{r}t)]_{t=t_0} \neq \text{const.} \quad (9)$$

From this inequality we shall deduce in a first step that the current densities $\mathbf{j}(\mathbf{r}t)$ and $\mathbf{j}'(\mathbf{r}t)$ corresponding to $v(\mathbf{r}t)$ and $v'(\mathbf{r}t)$ are different. In a second step it will be demonstrated that the densities $\rho(\mathbf{r}t)$ and $\rho'(\mathbf{r}t)$ are different.

Since we consider, by construction, only states $\Psi(t)$ and $\Psi'(t)$ that evolve from the same initial state Ψ_0 , the current densities \mathbf{j} and \mathbf{j}' as well as the densities ρ and ρ' are identical at the initial time t_0 :

$$\mathbf{j}(\mathbf{r}t_0) = \mathbf{j}'(\mathbf{r}t_0) = \langle \Psi_0 | \hat{\mathbf{j}}(\mathbf{r}) | \Psi_0 \rangle \equiv \mathbf{j}_0(\mathbf{r}), \quad (10)$$

$$\rho(\mathbf{r}t_0) = \rho'(\mathbf{r}t_0) = \langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle \equiv \rho_0(\mathbf{r}). \quad (11)$$

$\hat{\mathbf{j}}(\mathbf{r})$ denotes the paramagnetic current-density operator

$$\hat{\mathbf{j}}(\mathbf{r}) = -\frac{i}{2} \sum_{\sigma} \{ \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) [\nabla \hat{\psi}_{\sigma}(\mathbf{r})] - [\nabla \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r})] \hat{\psi}_{\sigma}(\mathbf{r}) \}, \quad (12)$$

and $\hat{\rho}(\mathbf{r})$ is the usual density operator

$$\hat{\rho}(\mathbf{r}) = \sum_{\sigma} \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}). \quad (13)$$

The time evolution of the current densities \mathbf{j} and \mathbf{j}' is most easily compared by means of the equations of motion

$$\frac{\partial}{\partial t} \mathbf{j}(\mathbf{r}t) = -i \langle \Psi(t) | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t)] | \Psi(t) \rangle \quad (14)$$

$$\frac{\partial}{\partial t} \mathbf{j}'(\mathbf{r}t) = -i \langle \Psi'(t) | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}'(t)] | \Psi'(t) \rangle. \quad (15)$$

Taking the difference of these two equations at the initial time t_0 one finds

$$\begin{aligned}\frac{\partial}{\partial t}[\mathbf{j}(\mathbf{r}t) - \mathbf{j}'(\mathbf{r}t)]_{t=t_0} &= -i \langle \Psi_0 | [\hat{\mathbf{j}}(\mathbf{r}), (\hat{H}(t_0) - \hat{H}'(t_0))] | \Psi_0 \rangle \\ &= -\rho_0(\mathbf{r}) \nabla (v(\mathbf{r}t_0) - v'(\mathbf{r}t_0)).\end{aligned}\quad (16)$$

If the potentials $v(\mathbf{r}t)$ and $v'(\mathbf{r}t)$ differ at $t = t_0$ (i.e., if Eq. (9) is satisfied for $k = 0$) then the right-hand side of Eq. (16) cannot vanish identically. Consequently $\mathbf{j}(\mathbf{r}t)$ and $\mathbf{j}'(\mathbf{r}t)$ will become different infinitesimally later than t_0 . If the minimum integer k for which Eq. (9) holds is greater than zero, one has to evaluate the $(k+1)$ th time-derivative of \mathbf{j} and \mathbf{j}' at t_0 . To this end, the quantum mechanical equation of motion

$$\frac{d}{dt} \langle \Psi(t) | \hat{O}(t) | \Psi(t) \rangle = \langle \Psi(t) | \frac{\partial}{\partial t} \hat{O}(t) - i[\hat{O}(t), \hat{H}(t)] | \Psi(t) \rangle$$

is applied $(k+1)$ times; the first time with $\hat{O}_1(t) = \hat{\mathbf{j}}(\mathbf{r})$, the second time with $\hat{O}_2(t) = -i[\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t)]$, etc. After some straightforward algebra one obtains

$$\begin{aligned}\frac{\partial^{k+1}}{\partial t^{k+1}} [\mathbf{j}(\mathbf{r}t) - \mathbf{j}'(\mathbf{r}t)]_{t=t_0} \\ = -\rho_0(\mathbf{r}) \nabla \left\{ \frac{\partial^k}{\partial t^k} [v(\mathbf{r}t) - v'(\mathbf{r}t)]_{t=t_0} \right\} \neq 0,\end{aligned}\quad (17)$$

where the last inequality follows from (9). Again the inequality (17) implies that $\mathbf{j}(\mathbf{r}t)$ and $\mathbf{j}'(\mathbf{r}t)$ will become different infinitesimally later than t_0 . This completes the proof for the current densities.

In order to prove that the densities $\rho(\mathbf{r}t)$ and $\rho'(\mathbf{r}t)$ are different, one employs the continuity equation:

$$\frac{\partial}{\partial t} [\rho(\mathbf{r}t) - \rho'(\mathbf{r}t)] = -\nabla \cdot [\mathbf{j}(\mathbf{r}t) - \mathbf{j}'(\mathbf{r}t)]. \quad (18)$$

Evaluating the $(k+1)$ th time-derivative of Eq. (18) at the initial time t_0 , one finds by insertion of Eq. (17)

$$\frac{\partial^{k+2}}{\partial t^{k+2}} [\rho(\mathbf{r}t) - \rho'(\mathbf{r}t)]_{t=t_0} = \nabla \cdot [\rho_0(\mathbf{r}) \nabla w_k(\mathbf{r})] \quad (19)$$

where

$$w_k(\mathbf{r}) \equiv \frac{\partial^k}{\partial t^k} [v(\mathbf{r}t) - v'(\mathbf{r}t)]_{t=t_0} = v_k(\mathbf{r}) - v'_k(\mathbf{r}). \quad (20)$$

It remains to be shown that the right-hand side of Eq. (19) cannot vanish identically if the condition (9), $w_k(\mathbf{r}) \neq \text{const}$, is satisfied. The proof is by *reductio ad absurdum*: Assume that the right-hand side of Eq. (19) vanishes and consider the integral

$$\int d^3r \rho_0(\mathbf{r}) [\nabla w_k(\mathbf{r})]^2 \quad (21)$$

which, by means of Green's theorem, can be written as

$$= -\int d^3r w_k(\mathbf{r}) \nabla \cdot [\rho_0(\mathbf{r}) \nabla w_k(\mathbf{r})] + \oint dS \cdot (\rho_0(\mathbf{r}) w_k(\mathbf{r}) \nabla w_k(\mathbf{r})). \quad (22)$$

As long as one deals with realistic, i.e. experimentally realizable potentials $v(\mathbf{r}t)$, the surface integral in (22) vanishes: Experimentally realizable potentials are always produced by real (this means, in particular, normalizable) external charge densities $\rho_{ext}(\mathbf{r}t)$ so that, in the Coulomb gauge,

$$v(\mathbf{r}t) = \int d^3r' \frac{\rho_{ext}(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|}. \quad (23)$$

A Taylor expansion of this equation about $t = t_0$ demonstrates that the expansion coefficients $v_k(\mathbf{r})$, and hence the functions $w_k(\mathbf{r})$, fall

off at least as $1/r$ asymptotically so that the surface integral vanishes. (For more general potentials see remark (iii) below.) The first term of (22), on the other hand, is zero by assumption. Thus the complete integral (21) vanishes and, since the integrand is nonnegative, one concludes

$$\rho_0(\mathbf{r})[\nabla w_k(\mathbf{r})]^2 = 0$$

in contradiction to $w_k(\mathbf{r}) \neq \text{const.}$ * This completes the proof of the theorem. A few remarks are in order at this point:

i) By virtue of the 1-1 correspondence established above (for a given Ψ_0), the time-dependent density determines the external potential uniquely up to within an additive purely time-dependent function. The potential, on the other hand, uniquely determines the time-dependent wave function, which can therefore be considered as a functional of the time-dependent density,

$$\Psi(t) = \Psi[\rho](t), \quad (24)$$

where $\Psi[\rho]$ is unique up to within a purely time-dependent phase factor. As a consequence, the expectation value of any quantum mechanical operator $\hat{Q}(t)$ is a unique functional of the density,

$$Q(t) = \langle \Psi[\rho](t) | \hat{Q}(t) | \Psi[\rho](t) \rangle \equiv Q[\rho](t); \quad (25)$$

the ambiguity in the phase of $\Psi[\rho]$ cancels out. As a particular example, the right-hand side of Eq. (14) can be considered as a density

* It is assumed here that $\rho_0(\mathbf{r})$ does not vanish on a set of positive measure. (Otherwise no contradiction is reached since $\rho_0(\mathbf{r})$ could be zero in exactly those regions of space where $w_k(\mathbf{r}) \neq \text{const.}$) Densities that vanish on a set of positive measure correspond to potentials having infinite barriers. Such potentials have to be excluded from the ordinary ground-state theory as well (see, e.g., Ref. 58).

functional which depends parametrically on \mathbf{r} and t :

$$P[\rho](\mathbf{r}t) \equiv -i \langle \Psi[\rho](t) | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t)] | \Psi[\rho](t) \rangle. \quad (26)$$

This implies that the time-dependent particle and current densities can always be calculated (in principle exactly) from a set of "hydrodynamical" equations:

$$\begin{aligned} \frac{\partial}{\partial t} \rho(\mathbf{r}t) &= -\nabla \cdot \mathbf{j}(\mathbf{r}t) \\ \frac{\partial}{\partial t} \mathbf{j}(\mathbf{r}t) &= P[\rho](\mathbf{r}t). \end{aligned} \quad (27)$$

In practice, the functional $P[\rho]$ is of course only approximately known.

ii) In addition to their dependence on the density, the functionals $Q[\rho]$, defined by Eq. (25), implicitly depend on the initial state Ψ_0 . No such state dependence exists in the ground state formalism. Of course one would prefer to have functionals of the density alone rather than functionals of $\rho(\mathbf{r}t)$ and Ψ_0 . It should be noted, however, that for a large class of systems, namely those where Ψ_0 is a non-degenerate ground state, $Q[\rho]$ is indeed a functional of the density alone. This is because any non-degenerate ground state Ψ_0 is a unique functional of its density $\rho_0(\mathbf{r})$ by virtue of the traditional HK theorem.¹ One has to emphasize that this class of systems also contains all cases of sudden switching where Ψ_0 is a ground state, but not the ground state of the initial potential $v(\mathbf{r}t_0)$.†

iii) It is essential for the proof of the 1-1 correspondence that the surface integral in (22) vanishes. As long as one considers only realistic physical potentials of the form (23), a vanishing surface integral is

† Whether an exclusive dependence on the density alone can be demonstrated for an even larger class of systems is an open question at present.

guaranteed. However, if one allows more general potentials, the surface integral does not necessarily vanish. Consider a given initial state Ψ_0 that leads to a certain asymptotic form of $\rho_0(\mathbf{r})$. Then one can always find potentials which increase sufficiently steeply in the asymptotic region such that the surface integral does not vanish. For such cases, the right-hand side of Eq. (19) can be zero, as was demonstrated by Xu and Rajagopal⁵⁹ (see also Dhara and Gosh⁶⁰) with the explicit examples

$$\rho_0(\mathbf{r}) = A e^{-\lambda r} / (\lambda r)^2, \quad w_k(\mathbf{r}) = B e^{\lambda r}, \quad A, \lambda > 0 \quad (28)$$

and

$$\rho_0(\mathbf{r}) = \text{const}, \quad w_k(\mathbf{r}) \text{ satisfying } \nabla^2 w_k(\mathbf{r}) = 0. \quad (29)$$

If one intends to include potentials other than those given by Eq. (23), an additional condition must be imposed to ensure that the surface integral in (22) vanishes. For a given initial state Ψ_0 , the allowable potentials must satisfy the condition*

$$\lim_{r \rightarrow \infty} \{r^2 \rho_0(\mathbf{r}) v_j(\mathbf{r}) \nabla v_j(\mathbf{r})\} = 0 \quad (30)$$

for all coefficients $v_j(\mathbf{r})$ of the Taylor expansion (4). Thus, the density functionals $Q[\rho]$ given by Eq. (25) not only depend explicitly on the initial state Ψ_0 ; the latter also determines the set of allowable potentials and hence the domain of densities for which the functionals $Q[\rho]$ are defined. One has to emphasize, however, that the cases excluded by the additional condition (30) are largely unphysical. The examples

* The condition $\rho_0 w_k \nabla w_k \rightarrow 0$, given by Dhara and Ghosh⁶⁰ for $r \rightarrow \infty$, is not sufficient to ensure a vanishing surface integral since it does not account for the fact that the spherical surface increment dS increases proportional to r^2 .

(28) and (29) of Xu and Rajagopal, for instance, lead to an infinite† potential energy $\int \rho(\mathbf{r}t)v(\mathbf{r}t)d^3r$ per particle in the vicinity of $t = t_0$. It would be desirable to prove the 1-1 correspondence under a physical condition, such as the requirement of a finite potential energy per particle, rather than under the more restrictive mathematical condition (30). Whether such a proof can be constructed is currently an open question.

2.2. Variational principle

The solution of the time-dependent Schrödinger equation (1) with initial condition (2) corresponds to a stationary point of the quantum mechanical action integral

$$A = \int_{t_0}^{t_1} dt \langle \Psi(t) | i \frac{\partial}{\partial t} - \hat{H}(t) | \Psi(t) \rangle . \quad (31)$$

Since there is a 1-1 mapping between time-dependent wave functions, $\Psi(t)$, and time-dependent densities, $\rho(\mathbf{r}t)$, the corresponding density functional

$$A[\rho] = \int_{t_0}^{t_1} dt \langle \Psi[\rho](t) | i \frac{\partial}{\partial t} - \hat{H}(t) | \Psi[\rho](t) \rangle \quad (32)$$

must have a stationary point at the correct time-dependent density (corresponding to the Hamiltonian $\hat{H}(t)$ and the initial state Ψ_0). Thus the correct density can be obtained by solving the Euler equation

$$\frac{\delta A[\rho]}{\delta \rho(\mathbf{r}t)} = 0 \quad (33)$$

with appropriate boundary conditions. The functional $A[\rho]$ can be

† Note that a function satisfying $\nabla^2 w_k(\mathbf{r}) = 0$ for all \mathbf{r} cannot vanish asymptotically (except in the trivial case $w_k(\mathbf{r}) \equiv 0$), nor can it approach a constant asymptotic value (except in the case $w_k(\mathbf{r}) \equiv \text{const}$).

written as

$$A[\rho] = B[\rho] - \int_{t_0}^{t_1} dt \int d^3r \rho(\mathbf{r}t) v(\mathbf{r}t) \quad (34)$$

with a universal (Ψ_0 -dependent) functional $B[\rho]$, formally defined as

$$B[\rho] = \int_{t_0}^{t_1} dt \langle \Psi[\rho](t) | i \frac{\partial}{\partial t} - \hat{T} - \hat{U} | \Psi[\rho](t) \rangle . \quad (35)$$

2.3. Time-dependent Kohn-Sham scheme

A particularly important application of the stationary action principle described in the last section is the derivation of a time-dependent KS scheme. To this end we first consider a system of non-interacting fermions subject to an external potential $v(\mathbf{r}t)$. The exact many-particle wave function is then a time-dependent Slater determinant $\Phi(t)$ which, by virtue of the Runge-Gross theorem, is a functional, $\Phi[\rho](t)$, of the time-dependent density. (Note that the argument of section 2.1 holds true for any particle-particle interaction U , in particular also for $U \equiv 0$. The functionals $P[\rho]$, $B[\rho]$, etc., however depend on the particular U considered.) The action functional for non-interacting particles then has the form

$$A_s[\rho] = B_s[\rho] - \int_{t_0}^{t_1} dt \int d^3r \rho(\mathbf{r}t) v(\mathbf{r}t) \quad (36)$$

where

$$B_s[\rho] = \int_{t_0}^{t_1} dt \langle \Phi[\rho](t) | i \frac{\partial}{\partial t} - \hat{T} | \Phi[\rho](t) \rangle . \quad (37)$$

According to the variational principle of section 2.2, the exact density can be obtained by solving the Euler equation

$$\frac{\delta A_s[\rho]}{\delta \rho(\mathbf{r}t)} = 0 = \frac{\delta B_s[\rho]}{\delta \rho(\mathbf{r}t)} - v(\mathbf{r}t). \quad (38)$$

Next we assume[†] that a single-particle potential $v_s(\mathbf{r}t)$ exists such that the interacting density is identical with the density

$$\rho(\mathbf{r}t) = \sum_{n=1}^N |\varphi_n(\mathbf{r}t)|^2 \quad (39)$$

of the non-interacting system described by the Schrödinger equation

$$i \frac{\partial}{\partial t} \varphi_n(\mathbf{r}t) = \left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}t) \right) \varphi_n(\mathbf{r}t). \quad (40)$$

If such a potential exists it must be unique (by virtue of the Runge-Gross theorem) and, in view of Eq. (38), it can be represented as

$$v_s(\mathbf{r}t) = \left. \frac{\delta B_s[\xi]}{\delta \xi(\mathbf{r}t)} \right|_{\xi(\mathbf{r}t)=\rho(\mathbf{r}t)}, \quad (41)$$

where the functional derivative of B_s has to be evaluated at the exact interacting (= non-interacting) density $\rho(\mathbf{r}t)$.

To determine the potential $v_s(\mathbf{r}t)$ more explicitly one employs the variational principle for the interacting system. First one rewrites the total action functional (34) as

$$\begin{aligned} A[\rho] = & B_s[\rho] - \int_{t_0}^{t_1} dt \int d^3r \rho(\mathbf{r}t) v(\mathbf{r}t) \\ & - \frac{1}{2} \int_{t_0}^{t_1} dt \int d^3r \int d^3r' \frac{\rho(\mathbf{r}t)\rho(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} - A_{xc}[\rho], \end{aligned} \quad (42)$$

where the "exchange-correlation" part of the action functional is formally defined as

[†] This assumption is analogous to the familiar assumption of simultaneous interacting and non-interacting v -representability made in the ground-state formalism.

$$A_{xc}[\rho] = B_s[\rho] - \frac{1}{2} \int_{t_0}^{t_1} dt \int d^3r \int d^3r' \frac{\rho(\mathbf{r}t)\rho(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} - B[\rho]. \quad (43)$$

Inserting (42) in the variational equation (33) one finds

$$\frac{\delta B_s[\rho]}{\delta \rho(\mathbf{r}t)} - [v(\mathbf{r}t) + \int d^3r' \frac{\rho(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta A_{xc}[\rho]}{\delta \rho(\mathbf{r}t)}] = 0. \quad (44)$$

Since this equation is solved only by the exact interacting density one obtains, by comparison with Eq. (41), the explicit representation

$$v_s(\mathbf{r}t) = v(\mathbf{r}t) + \int d^3r' \frac{\rho(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta A_{xc}[\rho]}{\delta \rho(\mathbf{r}t)}. \quad (45)$$

Eqs. (39), (40) and (45) constitute the time-dependent KS scheme. Compared to the time-dependent Hartree-fock method, this scheme has two advantages:

- a) The time-dependent effective potential $v_s(\mathbf{r}t)$ is local (i.e. a multiplication operator in real space).
- b) Correlation effects are included.

Explicit approximations for the time-dependent exchange-correlation potential

$$v_{xc}(\mathbf{r}t) = \frac{\delta A_{xc}[\rho]}{\delta \rho(\mathbf{r}t)} \quad (46)$$

will be discussed in section 3.2 in the context of linear response theory.

The density functionals $P[\rho]$, $B[\rho]$, $A_{xc}[\rho]$, etc, are well-defined only for "v-representable" densities, i.e., for densities that come from some time-dependent potential satisfying Eqs. (4) and (30). Since the restriction to v-representable densities is difficult to implement in the basic variational principle of section 2.2, a Levy-Lieb-type^{58,61,62} extension of the respective functionals to arbitrary (non-negative, normalizable) functions $\rho(\mathbf{r}t)$ appears desirable. Two different proposals

of this type have been put forward so far.^{63,64}

Besides these mathematical generalizations, a number of extensions of the time-dependent density-functional formalism to physically different situations have been developed. Those include spin-polarized systems,⁶⁵ multicomponent systems,⁶⁶ time-dependent ensembles,^{67,68} and external vector potentials.^{64,69}

3. FREQUENCY-DEPENDENT LINEAR RESPONSE

3.1. Selfconsistent equations for the linear density response

In this section we shall consider the ground-state response of electronic systems. In that case, the initial density $\rho_0(\mathbf{r})$ resulting from the potential $v_0(\mathbf{r})$ can be calculated from the ordinary (ground-state) KS scheme:

$$\left(-\frac{\nabla^2}{2} + v_0(\mathbf{r}) + \int d^3r' \frac{\rho_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[\rho_0](\mathbf{r})\right) \varphi_i^{(0)}(\mathbf{r}) = \epsilon_i \varphi_i^{(0)}(\mathbf{r}) \quad (47)$$

$$\rho_0(\mathbf{r}) = \sum_{i(occ)} |\varphi_i^{(0)}(\mathbf{r})|^2. \quad (48)$$

At $t = t_0$ a time-dependent perturbation $v_1(\mathbf{r}t)$ is switched on, i.e. the total external potential is given by

$$v(\mathbf{r}t) = \begin{cases} v_0(\mathbf{r}) & \text{for } t < t_0 \\ v_0(\mathbf{r}) + v_1(\mathbf{r}t) & \text{for } t \geq t_0. \end{cases} \quad (49)$$

Our goal is to calculate the linear density response $\rho_1(\mathbf{r}t)$ which is conventionally expressed in terms of the full response function χ as

$$\rho_1(\mathbf{r}t) = \int d^3r' \int_0^\infty dt' \chi(\mathbf{r}t, \mathbf{r}'t') v_1(\mathbf{r}'t'). \quad (50)$$

Since the time-dependent KS equations (39), (40), (45) provide a formally exact way of calculating the time-dependent density, the exact

linear density response of the interacting system can alternatively be calculated as the density response of the non-interacting KS system:

$$\rho_1(\mathbf{r}t) = \int d^3r' \int_{t_0}^{\infty} dt' \chi_{KS}(\mathbf{r}t, \mathbf{r}'t') v_s^{(1)}(\mathbf{r}'t'). \quad (51)$$

$v_s^{(1)}(\mathbf{r}t)$ is the time-dependent KS potential (45), calculated to first order in the perturbing potential. It can be written in the form

$$\begin{aligned} v_s^{(1)}(\mathbf{r}t) = & v_1(\mathbf{r}t) + \int d^3r' \frac{\rho_1(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} \\ & + \int d^3r' \int dt' f_{xc}(\mathbf{r}t, \mathbf{r}'t') \rho_1(\mathbf{r}'t'). \end{aligned} \quad (52)$$

f_{xc} denotes the exchange-correlation response kernel which is formally defined as the functional derivative of the time-dependent exchange-correlation potential (46),

$$f_{xc}(\mathbf{r}t, \mathbf{r}'t') = \left. \frac{\delta v_{xc}[\rho](\mathbf{r}t)}{\delta \rho(\mathbf{r}'t')} \right|_{\rho = \rho_0}, \quad (53)$$

evaluated at the initial ground-state density $\rho_0(\mathbf{r})$.

Eqs. (51) and (52) constitute the KS equations for the linear density response. Given some approximation for the exchange-correlation kernel f_{xc} , these equations provide a selfconsistent scheme to calculate the density response $\rho_1(\mathbf{r}t)$.

The response function χ_{KS} is relatively easy to calculate^{35,70} (as opposed to the full response function χ). In terms of the stationary KS orbitals of Eq. (47), the Fourier transform of $\chi_{KS}(\mathbf{r}t, \mathbf{r}'t')$ with respect to $(t-t')$ is given by

$$\chi_{KS}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{k,j} (f_k - f_j) \frac{\varphi_k^{(0)}(\mathbf{r})^* \varphi_j^{(0)}(\mathbf{r}) \varphi_j^{(0)}(\mathbf{r}')^* \varphi_k^{(0)}(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_k) + i\delta} \quad (54)$$

where f_k and f_j are Fermi occupation factors. The summations in

(54) run over all KS orbitals (including the continuum states).

For the purpose of constructing approximations to the exchange-correlation kernel f_{xc} , it is useful to express this quantity in terms of the full response function χ . A formally exact representation of f_{xc} is readily obtained by solving Eq. (50) for v_1 and inserting the result in (52). Eq. (51) then yields

$$f_{xc}(rt, r't') = \chi_{KS}^{-1}(rt, r't') - \chi^{-1}(rt, r't') - \frac{\delta(t-t')}{|r-r'|}. \quad (55)$$

By virtue of the Runge-Gross theorem, two potentials

$$v(rt) = v_0(r) + v_1(rt) \quad \text{and} \quad v'(rt) = v_0(r) + v'_1(rt)$$

always lead to different densities $\rho(rt)$ and $\rho'(rt)$ provided that $v_1(rt) \neq v'_1(rt) + c(t)$. This statement does not automatically imply that the linear density responses $\rho_1(rt)$ and $\rho'_1(rt)$ produced by $v_1(rt)$ and $v'_1(rt)$ are different; the difference between $\rho(rt)$ and $\rho'(rt)$ might show up only in higher perturbative orders. However, since the right-hand side of Eq. (19) is manifestly of first order in the perturbation, $\rho_1(rt)$ and $\rho'_1(rt)$ must in fact be different. Therefore the time-dependent KS scheme for the linear density response (Eqs. (51) and (52)) is well-defined and the inverse response operators χ^{-1} and χ_{KS}^{-1} in Eq. (55) must exist⁷¹ on the set of v -representable densities that correspond to the set of external potentials specified in Sec. 2.1. On a larger set of potentials, the response functions χ and χ_{KS} are not necessarily invertible. In particular, the frequency-dependent response operators $\chi(r, r'; \omega)$ and $\chi_{KS}(r, r'; \omega)$ cannot always be inverted since they determine, by definition, the linear density response to adiabatically switched monochromatic perturbations,

$$v_1(rt) = v_1(r\omega) e^{-i\omega t} e^{-\eta|t|}, \quad -\infty \leq t \leq \infty,$$

which are not covered by the Runge-Gross theorem (due to the condition (4)). As a matter of fact, it has been demonstrated^{72,73} that the response function $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ of suitably constructed non-interacting systems can have eigenvectors with vanishing eigenvalues at isolated frequencies ω_0 . Consequently the adiabatic density response vanishes at these frequencies and $\chi(\mathbf{r}, \mathbf{r}'; \omega_0)$ is not invertible.

We conclude this section with a discussion of the homogeneous electron gas, perturbed by an adiabatically switched potential consisting of a single Fourier component in $(q\omega)$ -space:

$$v_1(\mathbf{r}t) = e^{i(\mathbf{q} \cdot \mathbf{r} - \omega t)} v_1(q\omega) e^{-\eta|t|}, \quad -\infty \leq t \leq \infty.$$

Again the Runge-Gross theorem is not applicable in this case. However, for this particular system the exchange-correlation kernel can be constructed in explicit terms: The linear density response $\rho_1(q\omega)$ resulting from the perturbation $v_1(q\omega)$ is determined by the full response function $\chi^{hom}(q\omega)$ of the homogeneous electron gas,

$$\rho_1(q\omega) = \chi^{hom}(q\omega) v_1(q\omega). \quad (56)$$

Defining

$$f_{xc}^{hom}(q\omega) \equiv \frac{1}{\chi_0(q\omega)} - \frac{1}{\chi^{hom}(q\omega)} - \frac{4\pi}{q^2} \quad (57)$$

with χ_0 being the Lindhard function, one finds by insertion in (56):

$$\rho_1(q\omega) = \chi_0(q\omega) \{ v_1(q\omega) + \frac{4\pi}{q^2} \rho_1(q\omega) + f_{xc}^{hom}(q\omega) \rho_1(q\omega) \}. \quad (58)$$

Comparison of Eq. (58) with Eqs. (51)-(52) shows that the Fourier transform $f_{xc}^{hom}(\mathbf{r} - \mathbf{r}', t - t')$ of $f_{xc}^{hom}(q\omega)$ is indeed the exchange-

correlation kernel of the homogeneous electron gas. $f_{xc}^{hom}(q\omega)$ is closely related to the so-called local field correction $G(q\omega)$ of the homogeneous electron gas:

$$f_{xc}^{hom}(q\omega) = -\frac{4\pi}{q^2} G(q\omega). \quad (59)$$

Using well-known features of the electron gas response functions, f_{xc}^{hom} can be shown to have the following exact properties:

1. As a consequence of the compressibility sum rule one finds⁷⁴

$$\lim_{q \rightarrow 0} f_{xc}^{hom}(q, \omega = 0) = \frac{d^2}{d\rho^2}(\rho \epsilon_{xc}(\rho)) \equiv f_0(\rho), \quad (60)$$

where $\epsilon_{xc}(\rho)$ denotes the exchange-correlation energy per particle of the homogeneous electron gas.

2. The third-frequency-moment sum rule leads to⁷⁵

$$\begin{aligned} & \lim_{q \rightarrow 0} f_{xc}^{hom}(q, \omega = \infty) \\ &= -\frac{4}{5} \rho^{2/3} \frac{d}{d\rho} \left(\frac{\epsilon_{xc}(\rho)}{\rho^{2/3}} \right) + 6 \rho^{1/3} \frac{d}{d\rho} \left(\frac{\epsilon_{xc}(\rho)}{\rho^{1/3}} \right) \equiv f_{\infty}(\rho). \end{aligned} \quad (61)$$

3. According to the best estimates^{76,77} of $\epsilon_{xc}(\rho)$, the following relation holds for all densities

$$f_0(\rho) < f_{\infty}(\rho) < 0. \quad (62)$$

4. In the static limit ($\omega = 0$), the short-wavelength behavior is given by⁷⁸

$$\lim_{q \rightarrow \infty} f_{xc}^{hom}(q, \omega = 0) = -\frac{4\pi}{q^2}(1 - g(0)), \quad (63)$$

where $g(r)$ denotes the pair correlation function.

5. For frequencies $\omega \neq 0$, the short-wavelength behavior is⁷⁹

$$\lim_{q \rightarrow \infty} f_{xc}^{hom}(q, \omega \neq 0) = -\frac{2}{3} \cdot \frac{4\pi}{q^2}(1 - g(0)). \quad (64)$$

6. $f_{xc}^{hom}(q\omega)$ is a complex-valued function satisfying the symmetry relations

$$Re f_{xc}^{hom}(q, \omega) = Re f_{xc}^{hom}(q, -\omega) \quad (65)$$

$$Im f_{xc}^{hom}(q, \omega) = -Im f_{xc}^{hom}(q, -\omega). \quad (66)$$

7. $f_{xc}^{hom}(q\omega)$ is an analytic function of ω in the upper half of the complex ω -plane and approaches a real function $f_{\infty}(q)$ for $\omega \rightarrow \infty$.⁸⁰ Therefore, the function $f_{xc}^{hom}(q\omega) - f_{\infty}(q)$ satisfies standard Kramers-Kronig relations:

$$Re f_{xc}^{hom}(q\omega) - f_{\infty}(q) = P \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{Im f_{xc}^{hom}(q\omega')}{\omega' - \omega} \quad (67)$$

$$Im f_{xc}^{hom}(q\omega) = -P \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{Re f_{xc}^{hom}(q\omega') - f_{\infty}(q)}{\omega' - \omega}. \quad (68)$$

8. The imaginary part of f_{xc}^{hom} exhibits the high-frequency behavior

$$\lim_{\omega \rightarrow \infty} Im f_{xc}^{hom}(q, \omega) = -\frac{c}{\omega^{3/2}}. \quad (69)$$

for any $q < \infty$.⁸¹ A second-order perturbation expansion^{81,82} of the irreducible polarization propagator leads to the high-density limit

$$c = 23\pi/15. \quad (70)$$

9. In the same limit, the real part of f_{xc}^{hom} behaves like⁸³

$$\lim_{\omega \rightarrow \infty} \text{Re } f_{xc}^{hom}(q, \omega) = f_{\infty}(q) + \frac{c}{\omega^{3/2}}. \quad (71)$$

Since $c > 0$, the infinite-frequency value f_{∞} is approached from above. This implies, in view of the relation (62), that $\text{Re } f_{xc}^{hom}(q = 0, \omega)$ cannot grow monotonically from f_0 to f_{∞} .

The above features of f_{xc}^{hom} are valid for a three-dimensional electron gas. Analogous results have been obtained for the two-dimensional case.^{81,84,85}

3.2. Approximations for the exchange-correlation kernel

The time-dependent density-functional formalism described in section 2 can be shown⁵¹ to reduce to the traditional HKS formalism for the class of static initial value problems in which the potential is time-independent, $v(\mathbf{r}t) = v(\mathbf{r})$, and where the initial state Ψ_0 is the ground state of $v(\mathbf{r})$. In particular, the functional $A_{xc}[\rho]$ reduces to the usual exchange-correlation energy if ground-state densities are inserted for $\rho(\mathbf{r}t)$:

$$A_{xc}[\bar{\rho}] = (t_1 - t_0) \cdot E_{xc}[\bar{\rho}] \quad \text{for all ground-state densities } \bar{\rho}(\mathbf{r}). \quad (72)$$

This has an immediate consequence for possible approximations to the functional $A_{xc}[\rho]$: If an approximate expression for $A_{xc}[\rho]$ both satisfies (72) and is local in time, it must necessarily have the form

$$\int_{t_0}^{t_1} dt E_{xc}[\rho] \Big|_{\rho=\rho(\mathbf{r}t)}. \quad (73)$$

Of particular interest is the adiabatic local density approximation

$$A_{xc}^{ALDA}[\rho] \equiv \int_{t_0}^{t_1} dt \int d^3r [\rho \cdot \epsilon_{xc}(\rho)] \Big|_{\rho=\rho(\mathbf{r}t)} \quad (74)$$

which is local in time and space. By Eqs. (46) and (53), the exchange-correlation kernel corresponding to (74) takes the form

$$f_{xc}^{ALDA}(\mathbf{r}t, \mathbf{r}'t') = \delta(t-t') \delta(\mathbf{r}-\mathbf{r}') \frac{d^2}{d\rho^2} [\rho \cdot \epsilon_{xc}(\rho)] \Big|_{\rho=\rho_0(\mathbf{r})}. \quad (75)$$

Obviously, the static exchange-correlation energy can be expected to be a good approximation only for very slow time-dependent processes, i.e., one implicitly invokes an adiabatic approximation. This is also reflected in the fact that (75) is identical with the zero-frequency limit (60) of the homogeneous exchange-correlation kernel:

$$f_{xc}^{ALDA}(\mathbf{r}, \mathbf{r}'; \omega) = \delta(\mathbf{r}-\mathbf{r}') f_{xc}^{hom}(q=0, \omega=0; \rho) \Big|_{\rho=\rho_0(\mathbf{r})}. \quad (76)$$

Going beyond the adiabatic local density approximation, Gross and Kohn⁸³ have proposed an approximation for the exchange-correlation kernel which explicitly incorporates the frequency dependence. With respect to spatial coordinates, a local approximation as in (76) is employed:

$$f_{xc}^{LDA}(\mathbf{r}, \mathbf{r}'; \omega) = \delta(\mathbf{r}-\mathbf{r}') f_{xc}^{hom}(q=0, \omega; \rho) \Big|_{\rho=\rho_0(\mathbf{r})}. \quad (77)$$

The frequency-dependence of $Im f_{xc}^{hom}(q=0, \omega)$ is approximated by a Padé-like interpolation between the high- and the low-frequency limits:

$$Im f_{xc}^{hom}(q=0, \omega) = \frac{a(\rho) \cdot \omega}{(1 + b(\rho) \cdot \omega^2)^{5/4}} \quad (78)$$

where

$$a(\rho) = -c(\gamma/c)^{5/3}(f_{\infty}(\rho) - f_0(\rho))^{5/3}$$

$$b(\rho) = (\gamma/c)^{4/3}(f_{\infty}(\rho) - f_0(\rho))^{4/3}$$

$$\gamma = \frac{[\Gamma(1/4)]^2}{4\sqrt{2\pi}}.$$

f_0 , f_{∞} , and c are given by Eqs. (60), (61), and (70), respectively. For the exchange-correlation energy $\epsilon_{xc}(\rho)$ (which enters f_0 and f_{∞}), the parametrization of Vosko, Wilk and Nusair⁷⁷ is employed. Using the Kramers-Kronig relation (67), the real part can be expressed as

$$\begin{aligned} & Re f_{xc}^{hom}(q=0, \omega) \\ &= f_{\infty} + \frac{a}{\pi s^2} \cdot \sqrt{\frac{8}{b}} \cdot [2E(1/\sqrt{2}) - \frac{1+s}{2} \Pi(\frac{1-s}{2}, \frac{1}{\sqrt{2}}) \\ &- \frac{1-s}{2} \Pi(\frac{1+s}{2}, \frac{1}{\sqrt{2}})], \quad s^2 = 1 + b\omega^2. \end{aligned} \quad (79)$$

E and Π are complete elliptic integrals of the second and third kind in the standard notation of Byrd and Friedman.⁸⁶

Figs. 1 and 2 show the real and imaginary part of f_{xc}^{hom} as calculated from (78) and (79). The functions are plotted for the two density values corresponding to $r_s = 2$ and $r_s = 4$. For the lower density value ($r_s = 4$), a considerable frequency-dependence is found. The dependence on ω becomes less pronounced for higher densities. In the extreme high-density limit, the difference between f_0 and f_{∞} tends to zero. One finds the exact result

$$f_{\infty} - f_0 \sim r_s^2 \quad \text{for } r_s \rightarrow 0. \quad (80)$$

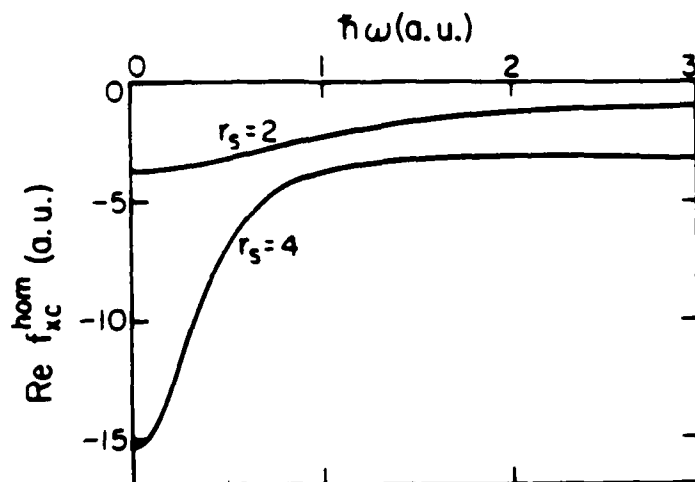


Fig. 1. Real part of the parametrization for $f_{xc}^{hom}(q=0, \omega)$ (from Ref. 75).

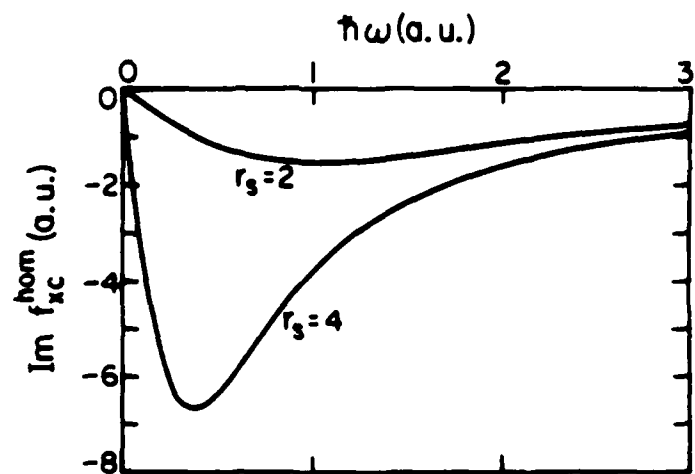


Fig. 2. Imaginary part of the parametrization for $f_{xc}^{hom}(q=0, \omega)$ (from Ref. 75).

At the same time, the depth of the minimum of $Im f_{xc}^{hom}$ decreases, again proportional to r_s^2 .

We finally mention that an extension of the parametrization (78) to nonvanishing q was given by Dabrowski.⁸⁷ A similar interpolation for the exchange-correlation kernel of the 2-dimensional electron gas has been derived by Holas and Singwi.⁸¹

3.3. Applications

The time-dependent KS scheme defined by Eqs. (51) and (52) has been successfully applied to the photo-response of atoms^{35,88,89} and molecules,^{90,91} metallic⁹²⁻⁹⁸ and semiconductor⁹⁹ surfaces and, most recently, of bulk semiconductors.¹⁰⁰

In the present context, we restrict ourselves to sufficiently low radiation frequencies such that the wavelength is much larger than the atomic radius and that Compton scattering is negligible. In the case of atoms, this condition is satisfied for photon energies below $\approx 3 \text{ keV}$. Under these circumstances, the electric field across the atom can be assumed to be constant.

The potential $v_1(\mathbf{r}t)$ associated with a monochromatic spatially constant electric field in z -direction is given by

$$v_1(\mathbf{r}t) = E z \cos \omega t. \quad (81)$$

The induced density change, $\delta \rho(\mathbf{r}t)$, is most conveniently characterized by a series of multipole moments. The induced dipole moment,

$$p(t) = - \int z \delta \rho(\mathbf{r}t) d^3 r, \quad (82)$$

can be expanded as¹⁰¹

$$p(t) = \alpha(\omega) \cdot \mathbf{E} \cos \omega t + \frac{1}{2} \beta(0) : \mathbf{E} \mathbf{E} + \frac{1}{2} \beta(2\omega) : \mathbf{E} \mathbf{E} \cos 2 \omega t$$

$$+\frac{1}{4}\gamma(\omega) : \mathbf{EEE} \cos \omega t + \frac{1}{4}\gamma(3\omega) : \mathbf{EEE} \cos 3\omega t, \quad (83)$$

where the notation is meant to convey the tensorial character of the quantities α, β, γ . The first coefficient, α , is termed the (*dipole*) *polarizability*; β and γ denote the second- and third-order (*dipole*) *hyperpolarizabilities*. For ordinary laboratory fields, the electric dipole moment is adequately described by the polarizability α . In the presence of intense laser fields, hyperpolarizabilities up to γ have to be taken into account. Higher orders are negligible in present-day experiments. For spherically symmetric states β is zero.

If one considers only the linear term in Eq. (83)), the Fourier components $\rho_1(r\omega)$ of the first-order density shift $\rho_1(r,t)$ can be treated independently and the frequency-dependent polarizability is given by

$$\alpha(\omega) = -\frac{2}{E} \int z \rho_1(r\omega) d^3r. \quad (84)$$

By virtue of the Golden Rule, the photoabsorption cross section is then proportional to the imaginary part of $\alpha(\omega)$:

$$\sigma(\omega) = \frac{4\pi\omega}{c} \text{Im } \alpha(\omega). \quad (85)$$

Zangwill and Soven³⁵ have used the time-dependent KS scheme (51)-(52) to calculate the linear density response of rare-gas atoms to a perturbation of the form (81). For the exchange-correlation kernel f_{xc} they employed the adiabatic local density approximation (76). The resulting photoabsorption cross section (as calculated from Eqs. (84) and (85)) turns out to be in rather good agreement with experiment. As an example, we show in Fig. 3 the photoabsorption cross section of the Xe atom in the vicinity of the 4d threshold. A few general remarks are in order at this point:

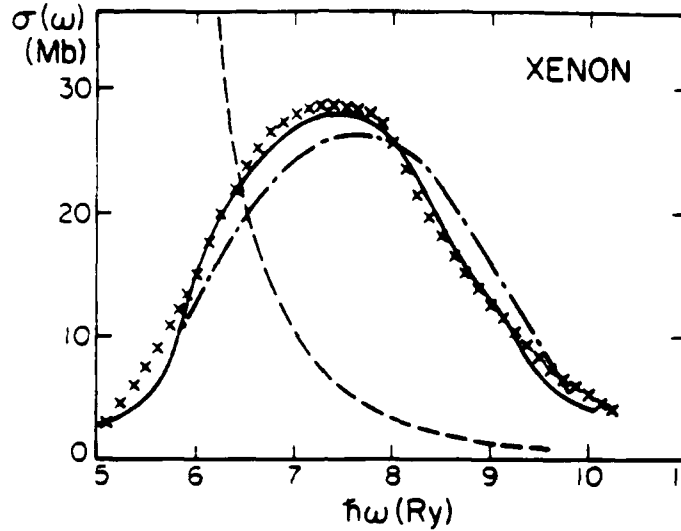


Fig. 3. Total photoabsorption cross section of the Xe atom versus photon energy in the vicinity of the 4d threshold (from Ref. 35). Solid line: selfconsistent time-dependent KS calculation; dash-dot line: selfconsistent time-dependent Hartree calculation ($f_{xc} \equiv 0$); dashed line: independent particle result (Hartree and exchange-correlation kernels neglected); crosses: experimental data from Ref. 102.

i) The calculations of Zangwill and Soven do not show the characteristic autoionization resonances found in high-precision measurements. This is due to the local density approximation employed for the ground-state exchange-correlation potential in Eq. (47). Since self-Coulomb and self-exchange energies do not properly cancel in the local density approximation, the total selfconsistent potential in Eq. (47) falls off exponentially rather than like $-1/r$. As a consequence, the effective potential does not support the high-lying Rydberg states essential for the description of autoionization resonances. In principle, the time-dependent KS scheme (51)-(52) should be capable of describing such effects if a selfinteraction-corrected approximation for the exchange-correlation potential is used. A different approach to the

selfinteraction problem was proposed by Zangwill and Soven in a second paper,⁸⁹ where they introduced selfenergy corrections directly in the response function χ_{KS} .

ii) Within the original scheme of Zangwill and Soven, the onset of continuous absorption for each atomic subshell is given by the corresponding KS single-particle energy eigenvalue. This follows directly from the fact that the response function χ_{KS} has poles at the KS single-particle excitation energies (cf. Eq. (54)). Since the KS excitation energies do not coincide with the exact atomic excitation energies, the calculated absorption edges are typically several volts below the observed thresholds. We emphasize that this result is due to the approximation (76) used for $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$. The exact function $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$, formally defined as the Fourier transform of (55), has a rather intricate structure which both removes the incorrect poles of χ_{KS} and gives rise to poles at the correct quasi-particle excitation energies.

iii) It is of interest to estimate the overall importance of the exchange-correlation kernel f_{xc} . The dash-dot curve in Fig. 3 shows the result obtained with f_{xc} set equal to zero. Deviations from the full calculation (solid curve) are about 10%. Clearly the full calculation agrees much better with the experimental values.

iv) Zangwill and Soven have employed the adiabatic local density approximation (76), in which $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$ is replaced by $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega = 0)$. On the basis of the parametrization (78)-(79) of Gross and Kohn,⁸³ the importance of the frequency dependence of the exchange-correlation kernel has been estimated: In the frequency range relevant for atomic photoabsorption, the ω -dependent function f_{xc} is expected⁷⁵ to differ by at most 2-6% from its zero-frequency value employed in the calculation of Zangwill and Soven. Since the complete neglect of f_{xc} leads to deviations of only 10%, the effect of the frequency-dependence of f_{xc} can be estimated to be smaller than 1% in the photoabsorption cross

section of atoms.

The scheme of Zangwill and Soven has also been applied to calculations of the photoabsorption of small molecules.^{90,91} In particular, a previously unexplained double-peak structure near 15 eV in the photoemission cross section of acetylene could be described successfully.

The adiabatic exchange-correlation functional (74) has also been employed in calculations of the third-order hyperpolarizabilities defined in Eq. (83). The results obtained by Zangwill¹⁰³ for rare-gas atoms are in good agreement with experiment. According to Senatore and Subbaswamy,¹⁰⁴ however, a term was missing in Zangwill's calculation. When they include this term, the agreement with experiment is reduced considerably: The calculated third-order hyperpolarizabilities of rare-gas atoms are too large typically by a factor of 2.

The response problem of surface electrons is to find the currents and charge densities induced by perturbing electromagnetic fields, and to calculate the resulting modifications of these fields.

The Hamiltonian governing the electronic dynamics is

$$\hat{H} \equiv \sum_i \frac{1}{2} (\mathbf{p}_i - \frac{1}{c} \mathbf{A}_1(\mathbf{r}_i, t))^2 + \sum_i (v_0(\mathbf{r}_i) + v_1(\mathbf{r}_i, t)) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (86)$$

where $v_0(\mathbf{r})$ is the potential due to the ion cores and $v_1(\mathbf{r}, t)$, $\mathbf{A}_1(\mathbf{r}, t)$ are the perturbing potentials in the transverse gauge ($\nabla \cdot \mathbf{A}_1 = 0$). The primary objective is to find the first-order density and current changes, $\rho_1(\mathbf{r}, t)$ and $\mathbf{j}_1(\mathbf{r}, t)$, caused by v_1 and \mathbf{A}_1 .

In most theoretical work, as well as in this section, the ionic potential, $v_0(\mathbf{r})$, is replaced by the potential due to a uniform positive charge background in a half-space, say $z > 0$. This is the so-called jellium model for metal surfaces. In this model there are two intrinsic microscopic length scales, the inverse Fermi wave-number, k_F^{-1} , and the Thomas-Fermi screening length (\approx surface thickness), κ_{TF}^{-1} . In the

present context, both lengths are typically of the order $a \approx 10^{-8}$ cm.

In the most important applications the perturbing potentials v_1 and A_1 vary on a length scale, ℓ , which satisfies $\ell \gg a$. Examples are the scalar potential $v_1(\mathbf{r})$ due to an external charge at a distance $z \gg a$, or the vector potential, $A_1(\mathbf{r}, t)$, associated with a light wave of wavelength $\lambda \gg a$. The corresponding n_1 and j_1 vary on the scale of ℓ in the x-y plane but, because of the abrupt drop of the unperturbed density at the surface (on the scale of a), they vary on the short scale a in the z-direction. Formal arguments due to Feibelman¹⁰⁵ have shown that, to leading order in a/ℓ , the effect of the surface on the electromagnetic fields far from the surface ($|z| \gg a$) is entirely characterized by two complex frequency-dependent lengths, $d_{\parallel}(\omega)$ and $d_{\perp}(\omega)$.

Actually, for the jellium model $d_{\parallel}(\omega) \equiv 0$.^{*} To define $d_{\perp}(\omega)$ we Fourier analyze all physical quantities parallel to the surface, in the x-y plane. For example, a Fourier component of the induced charge density becomes

$$\rho_1(\mathbf{r}, \omega) \equiv \rho_1(z, \omega) e^{i\mathbf{q}_{\parallel} \cdot \mathbf{r}}, \quad (87)$$

where $\mathbf{q}_{\parallel} = (q_x, q_y, 0)$ (and $|\mathbf{q}_{\parallel}| \cdot a \ll 1$). Then $d_{\perp}(\omega)$ is given by

$$d_{\perp}(\omega) \equiv \int z \rho_1(z, \omega) dz / \int \rho_1(z, \omega) dz, \quad (88)$$

i.e. it is the (complex) center of mass of the induced surface charge. $d_{\perp}(\omega)$ is the generalization of the static image plane introduced by Lang and Kohn.¹⁰⁶

This $d_{\perp}(\omega)$ is then the object of quantitative calculations. They

* This result has been obtained in the random phase approximation in Ref. 105. It is easily established as a rigorous many-body result for the jellium model (W. Kohn, unpublished).

require the density response, $\rho_1(z, \omega)$, to a uniform external electric field perpendicular to the surface. The calculation was first carried out in the random phase approximation (RPA), equivalent to time-dependent Hartree theory, in which effects of exchange and correlation are neglected in the self consistent perturbing potential (52). These calculations led to very interesting results not present in classical Maxwell theory, the surface photo effect, excitations of bulk and surface plasmons, and hints of an additional surface-localized plasmon. They help to explain experimental data on the photo-yield spectrum of Al.¹⁰⁷

Some recent calculations⁹²⁻⁹⁸ have employed the time-dependent response theory of Gross and Kohn, including exchange-correlation effects either within the adiabatic approximation (75) or the frequency-dependent parametrization (78)-(79). They have confirmed the qualitative conclusions of the RPA calculations, with quantitative modifications generally of the order of 10%.

Finally we mention some recent formal work on the response properties of real crystal surfaces (not the jellium model).¹⁰⁸ Here again the response properties of the surface are characterized by complex d -parameters having the dimension of a length. Quantitative calculations have been reported¹⁰⁸ to be in progress.

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